"The Combination of Hydrogen and Chlorine under the Influence of Light." By P. V. BEVAN, Trinity College, Cambridge. Communicated by Professor J. J. THOMSON, F.R.S. Received April 1,—Read May 14, 1903.

(Abstract.)

The present investigation was undertaken primarily to study the initial expansion observed when light is allowed to fall on a mixture of hydrogen and chlorine. This expansion was first noticed by Draper and studied more carefully by Pringsheim. The latter writer attributed the expansion to a dissociation of H_2 and Cl_2 molecules giving rise to a larger number of systems in the gas mixture than before illumination. For this part of the investigation the apparatus invented by Bunsen and Roscoe for determining the actinic properties of light was used. Bulbs considerably larger that Bunsen and Roscoe's were employed, admitting of more accurate determinations of small changes of volume. The expansion was found to be due to a rise in temperature, caused by the combination of hydrogen and chlorine to form hydrochloric acid. This rise in temperature was measured by the change of resistance of a fine platinum wire, sealed through the bulb, in which the gas mixture was exposed to light. The rise in temperature in all cases fully accounted for the initial expansion, and the rise in temperature was itself fully accounted for by the heat of formation of the hydrochloric acid produced. The initial expansion is thus shown to be only a side effect in the general case of the induction. The investigation then considers the period of induction. The action is shown to stop almost instantaneously on cutting off the light, so that combination only goes on while the light is continuously acting. The induction period or time in which the velocity of action has not reached its maximum value can be prolonged indefinitely, but its general character remains the same. The combination is made much more rapid by the presence of water vapour, and it seems probable that were the gases perfectly dry no action would take place.

If chlorine be first of all exposed to light, and then mixed with its own volume of hydrogen, the mixture shows a greater readiness to combine than if the chlorine had not been previously illuminated. This property is lost if the chlorine be bubbled through water after the preliminary illumination. Previous illumination of the hydrogen alone is without effect. The first step in the process of combination is thus an action between chlorine and water vapour or an action on chlorine alone. Some evidence as to the formation of an intermediate body is afforded by the production of a nucleus-forming substance in chlorine alone, and in the mixture of hydrogen and chlorine on which

a cloud can condense when the gas is submitted to a certain expansion. This cloud-forming substance appears before any hydrochloric acid is formed, and thus appears to be due to a true intermediate body.

The induction period, or period of acceleration of the action, is an essential part of the combination, and is to be attributed to the formation of intermediate compounds from water vapour and the two reacting gases. The nature of these compounds is not discovered, but the view is taken that they are molecular aggregates in which the individual atoms can come into each other's spheres of influence and so make intra-aggregate systems without much action on the whole individual, which can then break up, giving rise to the more stable systems, water and hydrochloric acid. This view of the process of the action can be shown to involve the qualitative characteristics of the initial stages of this particular action, and can be extended to actions in gaseous systems when the presence of a catalyser such as water vapour is necessary for the progress of the action at a finite rate. In the case of such actions a period of induction must be expected to occur, and the application of the law of mass action must be made with reference to the intermediate compounds formed with the catalyser. There is, therefore, no reason to expect that agreement will be found between the theory of mass action, as applied to the end-product equations, and the actual experimental results.